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BASIC MAGNESIUM CARBONATE

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EXOTHERMIC PROCESS IN THE DIFFERENTIAL THERMAL ANALYSIS CURVES OF  
BASIC MAGNESIUM CARBONATE

480-484\*

Hidehisa Hashimoto, Toshiaki Tomizawa, and Mamoru Mitomo

(Received 14 September 1967)

It is known that the differential thermal analysis (DTA) curve of basic magnesium carbonate exhibits an exothermic process. It was found in this study that this exothermic process was greatly affected by the atmosphere in which the decomposition reaction was carried out. This exothermic process and its cause were followed by DTA, thermogravimetric analysis (TGA), x-ray diffraction, and chemical analyses.

When basic magnesium carbonate is heated in air or nitrogen, it loses water in the temperature range 150-350°C to become amorphous magnesium carbonate. This amorphous carbonate begins to dissociate from about 400°C to become amorphous magnesium oxide. The crystallization of this amorphous oxide starts at about 505°C, and this is the source of this exothermic process. The exothermic process is much greater when the heating is conducted in an atmosphere of carbon dioxide. On the other hand, no exothermic process was seen when the heating was conducted under reduced pressure. The occurrence of the exothermic peak in the DTA curve and its magnitude are controlled by the ease at which CO<sub>2</sub> is released from within the amorphous oxide.

## 1 Introduction

When solid salts of the acid salts, basic salts, or hydroxides of metals are subjected to differential thermal analysis (DTA), there are some which exhibit not only a heat absorption peak but an exothermic peak as well. When salts of transition metals are heated, low oxides are formed by the thermolysis which is then often followed by an exothermic peak. This latter reaction, however, does not take place unless there is oxygen in the atmosphere. This is to say that the exothermic peak is not seen in an inert atmosphere. On the other hand, the salts of calcium and magnesium which do not belong to the above mentioned group frequently show both the heat absorption and heat release peaks.

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\*Numbers in the margin indicate pagination in the original foreign text.

Rao [1] observed exothermic peaks in the DTA curves of  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{ZnCO}_3$ , and  $\text{CdCO}_3$ . He concluded for the results of x-ray studies that the cause of this heat release was the amorphous oxide formed by the thermolysis being redeployed into a stable oxide lattice. Beck [2] made DTA studies of a number of Mg salts, and came to the same conclusion with Rao, however, his basis is not really clear. Dell and workers [3] made DTA studies of  $\text{MgCO}_3$ ,  $3\text{H}_2\text{O}$  and  $\text{MgO} \cdot \text{CO}_2(0.86) \cdot \text{H}_2\text{O}(1.39)$  and reported that part of the magnesite produced by the dehydration dissociated but a remainder was redeployed into a stable magnesite lattice. As a result, they explained there was excess energy being released to give this exothermic peak.

The studies mentioned have relied on small changes in the x-ray results upon which some rather bold conclusions were based, and the results thus far do not seem entirely conclusive. The authors focused their attention on the effect of the surrounding atmosphere on the exothermic peak in the DTA curve and studied the relation between the magnitude of this exothermic peak and the atmosphere as well as the relation between this atmosphere and the properties of the substance undergoing thermal changes. They employed DTA, thermogravimetric analysis (TGA), specific heat measurements, infrared spectral analysis, chemical analysis, and electron microscopy to the solution of this problem.

## 2 Experimental Procedure

The material used in this study was basic magnesium carbonate of reagent grade quality made by the Kanto Chemical Company. X-ray diffraction studies established its composition to be representable by  $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ .

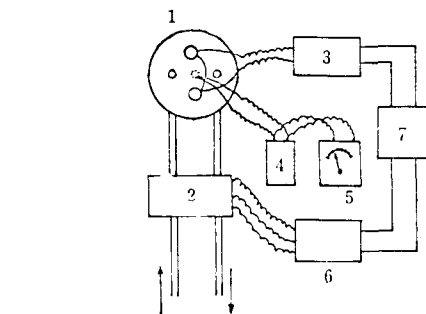
The following measurements were made first of all to see what changes this material underwent as it was heated continuously.

### 2.1 Differential thermal analysis (DTA)

A model HR-101 Galvanograph made by the Sanei Instrument Company was attached to a manual instrument made by the Mitamura Riken Company to fashion a self recording DTA unit. This instrument was operated at 5, 10, and  $15^\circ\text{C}/\text{min}$  heating rates to see what effect this rate of heating had on the DTA curves and particularly on the exothermic peak. Next, the effect of the atmosphere was looked into and the heating was conducted in air, nitrogen, carbon dioxide, or reduced pressure media. The heating rate here was standardized at  $10^\circ\text{C}/\text{min}$ .

Next, another DTA instrument was coupled to the detector unit of a gas chromatograph with the circuit of the type shown in Fig. 1 to analyze the effluent gas (EGA, effluent gas analyzer). This setup made possible the simultaneous recording of the DTA curve together with the determination of

the changes in the gas being released by thermolysis. This instrument made it possible to determine whether the heat absorption or release reaction was accompanied by gas release. It was not possible to discriminate between different gases with this setup. The carrier gas was air or nitrogen gas.



effluent gas

Figure 1. EGA-DTA setup

- 1: sample container, 2: released gas detector, 3: amplifier (DTA),  
 4: Dewar flask for cold reference, 5: thermometer, 6: bridge circuit,  
 7: two pen recorder

## 2.2 Thermogravimetric analysis (TGA)

A biological research type TGA instrument made by the Hamada Electric Company was used to determine the weight loss curve on heating. The rate of heating and atmosphere of heating were the same as for the DTA measurements.

## 2.3 Specific heat measurements

The changes in the specific heat of the starting material as it was being heated were determined with an adiabatic specific heat apparatus made by the Rigaku Electric Company. The atmosphere used here was air alone.

Comparing the various results of the measurements mentioned above, it is possible to get some insight to the processes of continuous changes taking place within the starting material but it is not possible to obtain quantitative data at the particular spot at which the change was taking place. In other words, information on items like the type and quantity of the crystalline phase, amount of amorphous phase, amount of carbonate, and amount of adsorbed gas were not obtainable. The special DTA apparatus mentioned was then used to see if it could supply this information, and DTA curves were recorded. Heatings at 10°C/min were carried out in a number of atmospheres. As soon as the sample reached the top prescribed temperature, it was quickly removed from the furnace and placed within dessicator where it was quick cooled. This was the material to be used in the studies to follow.

## 2.4 Microdiffusion analysis

It was felt that there would be some sort of bonding state between a portion of the gas expelled and the oxide at the point of appearance of the exothermic peak, and the extent of this bonding would show some relevancy so a microdiffusion analysis was made to check the carbonate source and the amount of CO<sub>2</sub> gas[4]. This method can be briefly described in the following manner. About 2-3 mg of sample which had been heated to the prescribed temperature in DTA apparatus and cooled was weighed accurately and placed within the outer chamber of the microdiffusion apparatus (made by Shibata Chemical Equipment Company). Also, some absorbing solution (0.01 N Ba(OH)<sub>2</sub>) and some decomposing solution (1 N H<sub>2</sub>SO<sub>4</sub>) were placed in this outer chamber after which the cover was replaced. This unit was then tilted in such a way that the sample made contact with the decomposing solution. After one hour standing, the barium hydroxide that was left was titrated with 0.1 N standard HCL solution through a microburet using 3:1 0.1% thymol blue-0.1% cresol red mixed indicator. The amount of CO<sub>2</sub> released was obtained by difference. The CO<sub>2</sub> initially present within the unit was determined by a blank run.

## 2.5 Infrared absorption spectrum

A Hitachi infrared spectrometer was used for the KBr disk determination of the infrared spectrum. Brucite (Mg(OH)<sub>2</sub>) and India magnesite (MgCO<sub>3</sub>) were used as standards for the -OH and -CO<sub>3</sub> absorptions. The standard reference for magnesia (MgO) was starting material which had been calcined one hour at 600°C.

## 2.6 X-ray diffraction

A model D-2 refractometer made by Rigaku Electric Company was used for the diffraction analysis. First of all, a qualitative analysis of the material before and after the appearance of each peak in the DTA curve was made. Next, a more detailed study was made of the amount of MgO crystal and the size of crystallites. The operating conditions were; target: CuK<sub>α</sub>, filter: Ni, potential: 25 kV, current: 10 mA, scanning speed: 1/2°/min, and time constant: 4 sec. The (220) diffraction profile of the MgO was used for the determination of the amount of MgO crystal and the crystallite size. The internal standard method [5] was used to determine the amount of crystal formed. The internal standard and sample were mixed in 1:2 ratio, and the area ratio taken from the diffraction profile was referred to a standard curve. Reagent grade KCl was the internal standard, and standard MgO was prepared by heating starting material three hours at 1500°C. The crystallite size was calculated from the half width of the diffraction profile [6].

## 2.7 Determination of specific area

The monomolecular adsorption of nitrogen at liquid nitrogen temperature was calculated from the BET equation using a least squares approach. The area occupied by one nitrogen molecule was taken to be 16.2 Å.

## 2.8 Electron microscope study

The material was dispersed in No. 4 varnish for observation under an electron microscope (Nippon Electron Company Superscope model 50) to study the morphology of the material before and after each peak. The direct magnification was 2000 times.

## 3 Results and Discussion

### 3.1 DTA

The rate of heating (5, 10, 15°C/min) has a great effect on the DTA curves. The heat absorption and release peaks shift upward with increasing rate of heating, and the net effect is a higher temperature for each phenomenon. There was, however, no exothermic peak observable when the heating rate was 5°C/min.

Next, the rate of heating was fixed at 10°C/min, and measurements were made under reduced pressure, air, nitrogen flow, and CO<sub>2</sub> atmospheres to see what effect the atmosphere had on the DTA curves. The results are shown in Fig. 2. About the same results were obtained from air or nitrogen as the surrounding atmosphere with heat absorptions being indicated at 110, 335, 450, and 520°C along with a sharp exothermic indication at 505°C. The heat absorption peaks appeared at lower temperatures when the heating was at reduced atmosphere, and no exothermic peak was seen. Compared to the curve in air, the curve in CO<sub>2</sub> atmosphere showed a larger heat absorption peak at 460°C which actually broke up into two steps. The heat absorption peak that followed the exothermic peak not only was shifted to the high temperature side but was also larger. The outstanding feature here is the fact that the exothermic peak here is very large compared to the other curves. This exothermic peak here appeared at 505°C just as was seen by the heating in air.

From the results described above in which the magnitude of the exothermic peak was the greatest in CO<sub>2</sub> atmosphere would suggest some relation between the partial pressure of CO<sub>2</sub> gas and the magnitude of this exothermic peak. On the other hand, the appearance of this peak in nitrogen or air atmosphere indicates that there is no direct interaction between CO<sub>2</sub> and the sample. The exothermic peak does not appear under reduced pressure and this fact coupled with the heat absorption process due to the dissociation of the carbonate salt is essentially complete at about 450°C indicate that the atmosphere for this exothermic reaction is created by the dissociation and

is related to the ease of release of  $\text{CO}_2$  held within the amorphous oxide. The ease of release of this  $\text{CO}_2$  seems to be related to the magnitude of this exothermic peak.

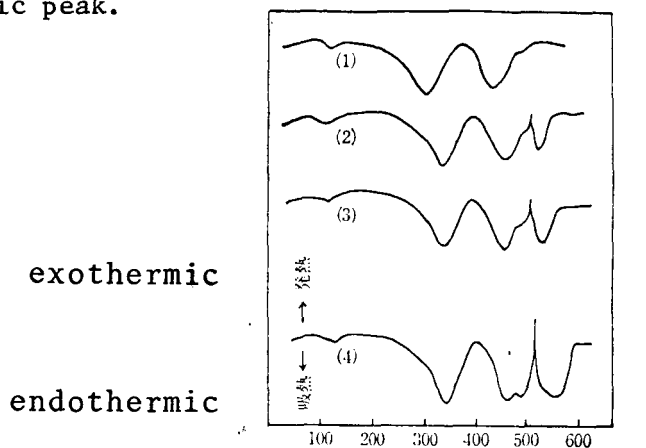


Figure 2. Relation between the DTA curve and atmosphere

(1): under reduced atmosphere, (2) in nitrogen, (3) in air, (4) in  $\text{CO}_2$  gas

The simultaneous determination of the EGA-DTA curves is shown in Fig. 3. These results were obtained in air. The water formed by this dissociation condensed within the lines and could not be detected (some water was recovered when the connecting lines were placed within the thermostat). The starting material releases water and  $\text{CO}_2$  by thermolysis, and the 450 and 520°C heat absorption peaks shown in Fig. 2 are the  $\text{CO}_2$  release peaks while the other endothermic peaks are associated with water release. It is also clear that the exothermic peak also is associated with  $\text{CO}_2$  release. On the other hand, it is difficult to conceive that a dissociation reaction is exothermic so that it is not the case that the cause for this exothermic peak is the release of  $\text{CO}_2$  by the dissociation.

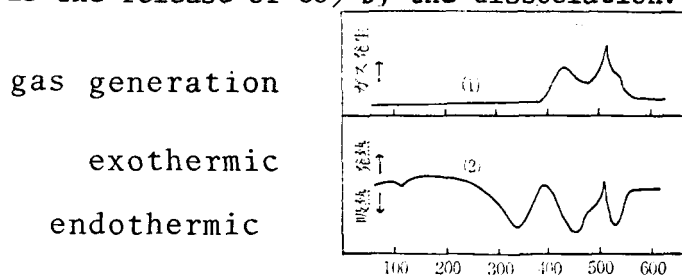


Figure 3. EGA-DTA curves (in air)

(1): EGA, (2): DTA

### 3.2 TGA

The TGA curve for the starting material is shown in Fig. 4. The ordinate is calibrated such that a completely dissociated material will register 100%. There is no simultaneous TGA and DTA determinations here so that it is unreasonable to make rigorous comparisons with the results of the study in which the heating rates were varied, however, there is good agreement where the DTA endothermic peak and the sharp loss in weight appear. At the section where the exothermic peak appears there is a decreased rate of weight loss before and after the peak, but there is a continuous loss in weight, and there is good agreement with the exothermic peak of  $\text{CO}_2$  release seen in the EGA curve.

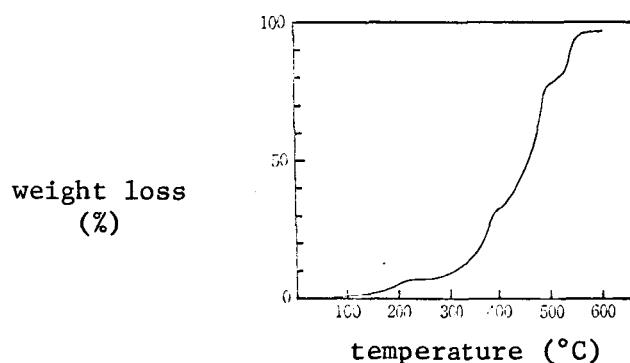


Figure 4. Curve showing weight loss of starting material on heating

### 3.3 Specific heat curve

The results of measurements in air are shown in Fig. 5. It would seem that the three peaks seen here correspond to the endothermic processes at 335, 450, and 520°C but there is actually a significant shift to the lower temperatures in each peak. It is thought that should there be a lowering in temperature due to the heat of reaction in the specific heat measurement, there will be a stagnation before the temperature begins to rise. In contrast, the DTA uses a linear rate of heating. The two peaks on the higher side of the specific heat determinations may be thought to correspond to the 450 and 520°C endothermic peaks of the DTA curve which are associated with two separate reactions that take place at separate temperatures. Both reactions release  $\text{CO}_2$  gas, but the mechanism is apparently different. The ordinate here is calibrated in the time (sec) required to raise the sample temperature by 1°C.



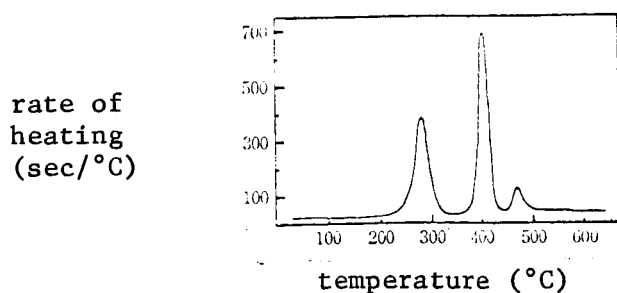


Figure 5. Specific heat curve of starting material

### 3.4 Microdiffusion analysis

The carbonate content and the adsorbed  $\text{CO}_2$  in mols were determined for the sample removed from the DTA apparatus. This sample had partially undergone weight loss due to heating such that there was difference in the composition of the sample between runs, and the sample weight versus mols  $\text{CO}_2$  between runs could not be compared. As a result, the ratios between the mols  $\text{CO}_2$  versus mols  $\text{MgO}$  in the samples were determined, and these changes are compared in Fig. 6. The mols  $\text{MgO}$  was determined by taking a portion of the sample that had been used for the  $\text{CO}_2$  determinations and heating it until it was completely dissociated.

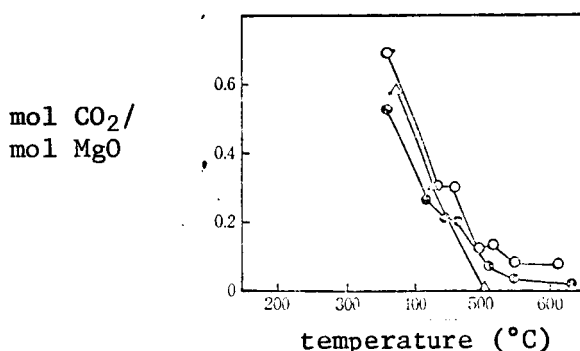


Figure 6. Changes in  $\text{CO}_2$  content of sample  
 -o-: in  $\text{CO}_2$  gas, -□-: in air, -Δ-: under reduced pressure

The changes in  $\text{CO}_2$  content decreased monotonously with rising temperature under reduced pressure. There was a drop in the rate of weight decrease near  $440\text{--}460^\circ\text{C}$  when the heating was in air to be followed by a sharp drop again at about  $510^\circ\text{C}$ . There is also a rapid drop in weight on heating in  $\text{CO}_2$ , but here again this rate of loss slackens near  $440\text{--}470^\circ\text{C}$  just as in air followed by resumed rapid rate of weight decrease along about  $500^\circ\text{C}$ . The rate of decrease became smaller in both air and  $\text{CO}_2$ . The  $\text{CO}_2$  content of the sample before the exothermic peak was greatest when the heating was in  $\text{CO}_2$  followed by heating in air, and this content was the lowest in heating under reduced pressure. When the results of these analysis are

combined with the DTA results, it is seen that the magnitude of this exothermic peak is large when the  $\text{CO}_2$  content just before this peak is large, and the concept that this exothermic peak is larger the more difficult the separation of the  $\text{CO}_2$  released by the dissociation from the amorphous oxide is supported. On the other hand, the release of  $\text{CO}_2$  is not exothermic so this is not the direct cause of this peak.

### 3.5 Infrared absorption spectrum

The infrared absorption spectra of the starting sample, various heated samples,  $\text{MgO}$ , and  $\text{MgCO}_3$  are shown in Fig. 7. The spectrum of the starting material shows a two step peak near  $3500\text{ cm}^{-1}$ , a peak near  $1600\text{ cm}^{-1}$ , two sharp peaks at  $1480$  and  $1440\text{ cm}^{-1}$ , and small peaks at  $870$ ,  $840$ , and  $790\text{ cm}^{-1}$ . Heating to just below the endothermic peak at  $335^\circ\text{C}$  shows only the loss of the  $3500\text{ cm}^{-1}$  peak which is the only difference from the spectrum of the starting material although the overall absorption is smaller. The material heated to just below the  $450^\circ\text{C}$  endothermic peak gives a spectrum very similar to that of  $\text{MgCO}_3$ . Thus, it is clear that the endothermic peak at  $335^\circ\text{C}$  is associated with the reaction in which an  $-\text{OH}$  group is lost. The broad absorption at  $1540\text{ cm}^{-1}$  believed to be due to  $\text{CO}_2$  is seen to have decreased in the samples heated to  $440$ ,  $500$ , or  $520^\circ\text{C}$  which is believed to show the progress of the  $\text{CO}_2$  abstraction reaction. There is the indication of a  $\text{CO}_2$  type bonding in the sample heated to  $500^\circ\text{C}$  where the  $\text{CO}_2$  abstraction starting at  $450^\circ\text{C}$  as shown by the DTA curve is considered essentially complete just before the exothermic peak. This is not seen in the sample heated to  $520^\circ\text{C}$ .

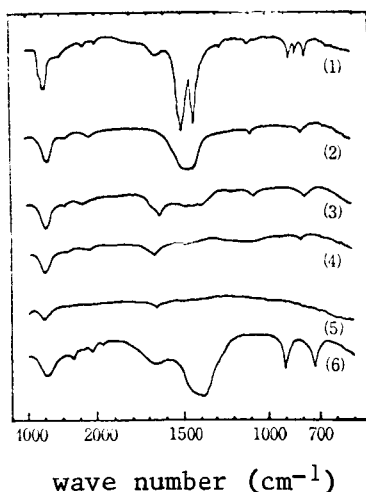


Figure 7. Infrared absorption spectra

(1) starting material, (2), (3), (4): heated to  $440$ ,  $500$ ,  $520^\circ\text{C}$ , (5):  $\text{MgO}$ ,  
(6):  $\text{MgCO}_3$

### 3.6 X-ray analysis

Qualitative analyses were made of the samples just before and after each endothermic peak, and the diffraction pattern of material before the 335°C endothermic peak was little different from that of the starting sample. Heating to past the first endothermic peak at 370°C changes the diffraction pattern to what was considered an essentially amorphous material having just one very weak diffraction line at  $2\theta = 12.5^\circ$ . Heating past the 450°C endothermic peak gave very widely spread and weak absorption lines due to MgO, and this broadening narrowed with increasing line intensities as the temperature was made still higher. The diffraction lines reported by Dell et al. [7] to be the  $\text{MgCO}_3$  lines and which were considered to be the cause of the exothermic peak were not observed here. On the other hand, the formation of  $\text{MgCO}_3$  was observed near the exothermic peak in a separate experiment in the study of the thermolysis of basic magnesium carbonate ( $3 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$ ) prepared by the Murotani procedure [7]. It is evident that  $\text{MgCO}_3$  formation can result near the exothermic peak depending on the composition of the starting material, but the exothermic peak appears regardless of whether there is  $\text{MgCO}_3$  formation or not. As a result, the exothermic peak is thought to be unrelated to the formation of  $\text{MgCO}_3$ .

The relation between treatment atmosphere and crystallite size is shown in Fig. 8. This size is least when heating is under reduced pressure and slightly greater when the heating is in air. It is greatest when the heating is in  $\text{CO}_2$ . The crystallite size grew slowly with heating under reduced pressure or in air while there was a sharp increase in size just before the exothermic peak when the heating was in  $\text{CO}_2$ . This rate of growth slowed down considerably after the peak. It is intuitively assumed that the rapid growth in crystallite size just before the exothermic peak is one of the factors responsible for the appearance of this peak. It seems reasonable to assume that the release of surface energy as a result of crystallite growth is the driving force which brings about this exothermic process. On the other hand, very little growth was seen when a sample was heated in air for the DTA analysis in which the exothermic peak definitely appeared. The surface energy released in this instance was meager. As a result, there seems to be no relation between the exothermic peak and the release of surface energy when basic magnesium carbonate is subjected to DTA analysis.

The relation between the heating atmosphere and amount of MgO crystal is shown in Fig. 9. Heating in air resulted in high crystal ratio starting in at low temperature. The dissociation proceeds much more rapidly from low temperature in a reduced pressure atmosphere but the crystal ratio is less than in air. Crystallization is delayed when the heating is in  $\text{CO}_2$  medium, and MgO crystallization is not seen until the temperature is relatively high.

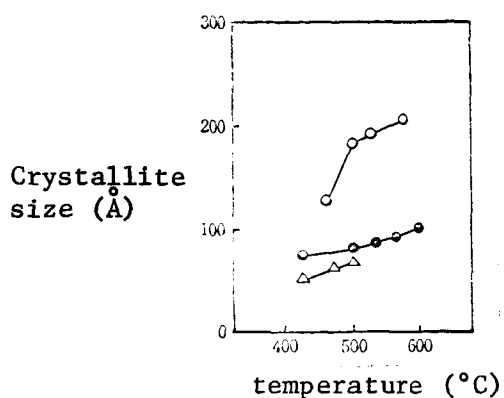


Figure 8. Relation between crystallite size and atmosphere (symbols same as in Fig. 6)

There is a sharp increase in the crystal ratio that accompanies rising temperature just before the exothermic peak when the heating is in  $\text{CO}_2$  or in air in which media the exothermic peak appears. The exothermic peak was greatest in  $\text{CO}_2$  gas in which crystallization was most rapid. On the other hand, the release of surface energy resulting from the increased  $\text{MgO}$  crystallite size which process is thought to be the factor responsible for the appearance of the exothermic peak and the crystallization of amorphous  $\text{MgCO}_3$  reported by Dell [3] cannot be considered in the same light. A larger  $\text{CO}_2$  partial pressure makes for a larger exothermic peak, and the results of the microdiffusion analysis indicated that this peak was larger the greater the residual  $\text{CO}_2$  just before this peak. These results indicate that the exothermic peak is larger the more difficult it is to remove the  $\text{CO}_2$  that is incorporated within the amorphous oxide. The phenomenon of  $\text{CO}_2$  release, however, cannot be taken to be the same as the exothermic process. When all the information derived thus far is combined with the conclusions of Rao [1] and Beck [3], it seems most reasonable to accept the concept that this exothermic process is due to the crystallization of amorphous oxide. On the other hand, no exothermic peak was seen during the heating under reduced pressure even though there was a degree of crystal growth here comparable to that resulting from heating in air. The DTA and EGA results showed definitely that heating in air was accompanied by two endothermic peaks at 445 and 520°C both before and after the exothermic peak which are associated with  $\text{CO}_2$  release. There is only one such peak when the heating is under reduced pressure, and this may somehow be the key to this problem. It would have been expected from the rate of crystal growth which was nearly the same as the rate in air that heating in vacuum would give a comparable exothermic peak. The microdiffusion analysis indicated that  $\text{CO}_2$  abstraction was readily carried out under reduced pressure, and this behavior must have some effect on the DTA curve such that no exothermic peak was observed. The various items mentioned above lead us to believe that the exothermic process that appears on the DTA curve of basic magnesium carbonate is due to the crystallization of amorphous oxide. In the actual situation, however, the

appearance of this exothermic peak and its magnitude are greatly affected by the ease at which  $\text{CO}_2$  incorporated within the amorphous oxide is removed.

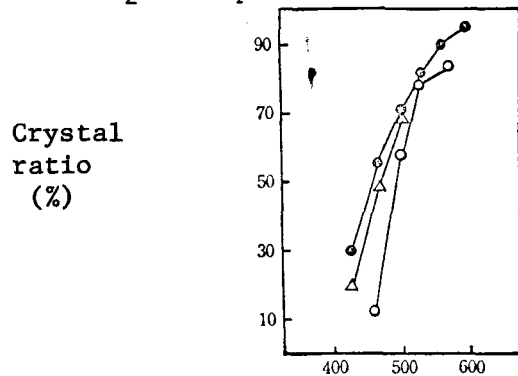


Figure 9. Relation between crystal ratio and atmosphere (symbols same as in Fig. 6)

### 3.7 Specific surface area

The results of specific surface area measurements are shown in Fig. 10. Maxima are observed in the curves for heating under reduced pressure and in air at about  $480^\circ\text{C}$  which is just after the dissociation reaction that releases  $\text{CO}_2$ . This maximum comes near  $520^\circ\text{C}$  when the heating is in  $\text{CO}_2$ . Generally speaking, the specific surface area is largest just after dissociation and decreases thereafter as the temperature is raised. The endothermic peaks before and after the exothermic peak which are associated with the  $\text{CO}_2$  release that are seen on the DTA curve are somewhat displaced to the high temperature side when the heating is in  $\text{CO}_2$  as compared to heating in air. This is thought to have caused the maximum in the specific surface area to have shifted to the high temperature direction.

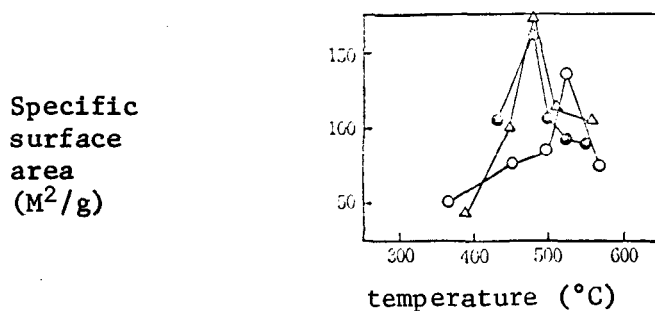


Figure 10. Relation between specific surface area and atmosphere (symbols same as in Fig. 6)

### 3.8 Electron microscope observations

All the samples with the different treatments showed the same shape as the starting material, and there was very little difference with the

temperature or the atmosphere of the heat treatment. Also no differences were noted just before and after the exothermic peak.

The above item was followed in a separate study, and the following general conclusion is possible. Heating the starting material results initially in a loss of water to form the amorphous magnesium carbonate. This material releases  $\text{CO}_2$  near  $450^\circ\text{C}$  with absorption of heat to form the amorphous magnesium oxide. Further heating converts this amorphous oxide to the crystalline oxide.

The exothermic process is thought to be due to the crystallization of magnesium carbonate, but it should be kept in mind that the appearance and the magnitude of the exothermic peak on the DTA curve are related to the ease with which the  $\text{CO}_2$  that is incorporated by the amorphous oxide is released. In other words, the exothermic peak is larger the more difficult this  $\text{CO}_2$  is to remove and smaller the more ready its removal. No exothermic peak is seen in vacuum in which  $\text{CO}_2$  is most easily removed.

This paper is Part 16 of the series "Thermal Dissociation Reaction Studies of Solids."

The preceeding paper of this series was Toshiaki Tomizawa, Hidehisa Hashimoto, Konchokichi Shigeki, Koka, 70, 2129 (1967).

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